

CLAIMS

1. A solid component of catalyst for the (co)polymerization of ethylene, comprising titanium, magnesium, chlorine, an organo-oxygenated protic compound  $D_p$ , and a neutral electron-donor aprotic compound D, in the following molar ratio ranges:  
 $Mg/Ti = 1.0-50$ ;  $D/Ti = 1.0-15$ ;  
 $Cl/Ti = 6.0-100$ ;  $D_p/D = 0.05-3$ .
2. The solid component according to claim 1, additionally comprising an inert solid I in a suitable granular form, in a quantity ranging from 10 to 90% by weight with respect to the total weight of the solid component.
3. The solid component according to claim 2, wherein said inert solid I is in a quantity ranging from 25 to 50% by weight.
4. The solid component according to any of the previous claims, wherein said inert solid I is selected from granular inorganic solids included in the group: silica, titania, silico-aluminates, calcium carbonate, magnesium chloride, having average dimensions of the granule ranging from 10  $\mu m$  to 300  $\mu m$ .
5. The solid component according to claim 4, wherein said solid I consists of microspheroidal silica having an average diameter ranging from 20 to 100  $\mu m$ , a BET sur-

face area ranging from 150 to 400 m<sup>2</sup>/g, a total porosity equal or higher than 80% and an average pore radius of 50 to 200 Å.

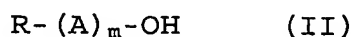
6. The solid component according to any of the previous claims, characterized by the following molar ratio ranges among the constituents:

$$\text{Mg/Ti} = 1.5-10; \quad \text{D/Ti} = 3.0-8.0;$$

$$\text{Cl/Ti} = 10-25; \quad \text{D}_p/\text{D} = 0.1-2.0.$$

7. The solid component according to any of the previous claims, wherein said ratio  $\text{D}_p/\text{D}$  ranges from 0.2 to 1.0

8. The solid component according to any of the previous claims, wherein said organo-oxygenated protic compound  $\text{D}_p$  is selected from compounds having the following formula (II):



wherein:

R is an aliphatic, cyclo-aliphatic or aromatic radical, optionally fluorinated, containing from 1 to 30 carbon atoms,

A is selected from divalent groups having the formula  $\text{CR}^1\text{R}^2$ , CO, SCO and SO, preferably CO or  $\text{CR}^1\text{R}^2$ , wherein each  $\text{R}^1$  and  $\text{R}^2$  is independently hydrogen or an aliphatic or aromatic group having from 1 to 10 carbon atoms;

m is 0 or 1.

9. The solid component according to any of the previous claims, wherein said organo-oxygenated protic compound D<sub>p</sub> is selected from aliphatic or aromatic, preferably aliphatic, alcohols and organic acids, having from 2 to 10 carbon atoms.
10. The solid component according to any of the previous claims, wherein said aprotic electron-donor compound D is a coordinating organic compound having from 3 to 20 carbon atoms, comprising at least one heteroatom selected from non-metallic compounds of groups 15 and 16, preferably at least one oxygen atom linked to a carbon atom.
11. The solid component according to any of the previous claims, wherein said electron-donor compound D is selected from compounds of the groups of ketones, ethers, esters, amines, amides, thioethers, and xanthates, linear or cyclic, aliphatic or aromatic, having from 4 to 10 carbon atoms.
12. The solid component according to any of the previous claims 10 or 11, wherein said compound D is selected from dibutyl ether, dihexyl ether, methylethyl ketone, diisobutyl ketone, tetrahydrofuran, dioxane, ethyl acetate, butyrolactone, preferably tetrahydrofuran.
13. The solid component according to any of the previous claims, wherein said titanium is present in a quantity

ranging from 1 to 10% by weight.

14. A process for the preparation of a solid component according to any of the previous claims from 1 to 13, comprising the following steps in succession:

5 (a) formation of a mixture and dissolution, in aprotic electron-donor compound D, of a magnesium chloride and a titanium compound having formula (I):



10 wherein each  $\text{R}^3$  represents a hydrocarbyl or acyl radical having from 1 to 15 carbon atoms;

each X is selected from chlorine, bromine or iodine;

v is 3 or 4, and represents the oxidation state of titanium,

a is a number ranging from 0 to v,

15 with a molar ratio between magnesium and titanium ranging from 1/1 to 50/1;

(b) partial separation of the compound D from said mixture prepared in step (a) until a residue is obtained, solid at room temperature, wherein the D/Ti ratio ranges from 1.5 to 40,

(c) formation of a suspension of said solid residue in a liquid hydrocarbon medium,

20 (d) addition to said suspension of an organo-oxygenated protic compound  $\text{D}_p$ , in such a quantity that the molar ratio  $\text{D}_p/\text{D}$  ranges from 0.1 to 1.2 and main-

taining the mixture until the desired solid component of catalyst is formed.

15. The process according to claim 14, wherein, in step (a) an inert solid I in a suitable granular form, is also added.

16. The process according to the previous claim 15, wherein said inert solid I is selected from granular inorganic solids included in the group: silica, titanium, silico-aluminates, calcium carbonate, magnesium chloride, having average granule dimensions ranging from 10  $\mu\text{m}$  to 300  $\mu\text{m}$ .

17. The process according to the previous claims 15 or 16, wherein said inert solid I consists of microspheroidal silica having an average diameter ranging from 20 to 100  $\mu\text{m}$ , a BET surface area ranging from 150 to 400  $\text{m}^2/\text{g}$ , a total porosity equal or higher than 80% and an average pore radius of 50 to 200  $\text{\AA}$ .

18. The process according to any of the previous claims from 14 to 17, wherein said titanium compound having formula (I) is essentially soluble in said compound D and is selected from titanium chlorides, bromides, alcoholates and carboxylates.

19. The process according to any of the previous claims from 14 to 17, wherein said compound having formula (I) in step (a) is titanium trichloride.

20. The process according to any of the previous claims from 14 to 19, wherein said magnesium chloride is in amorphous or semi-amorphous form.
- 5 21. The process according to any of the previous claims from 14 to 20, wherein, in said step (a), the atomic ratio between magnesium and titanium ranges from 1.0 to 50 and the ratio (D moles)/(Ti atoms) ranges from 5 to 100.
- 10 22. The process according to any of the previous claims from 14 to 21, wherein said step (a) is carried out at a temperature ranging from room temperature to the boiling point of the donor compound D, for a time varying from a few minutes to 24 hours, until at least 80% of said compounds of Ti and Mg have been dis-
- 15 solved.
23. The process according to any of the previous claims from 14 to 22, wherein said step (b) is carried out by means of evaporation, preferably by spray-drying.
- 20 24. The process according to any of the previous claims from 14 to 23, wherein the molar ratio  $D_p/D$  in said step (d) ranges from 0.2 to 1.2.
- 25 25. The process according to any of the previous claims from 14 to 24, wherein said step (d) is carried out by heating the mixture to a temperature ranging from 40 to 100°C, for a period of time varying from 5 minutes

to 5 hours.

26. The process according to claim 25, wherein the reaction mixture in said step (d) is heated to a temperature of 60 to 80°C, for a period ranging from 5 to 60 minutes.

27. A process for the preparation of a solid component according to any of the previous claims from 1 to 13, comprising the reaction in an inert liquid medium of a solid precursor containing titanium, magnesium, chlorine, an aprotic electron-donor compound D and optionally an inert solid compound I, in the following molar ratios between each other:

$Mg/Ti = 1-50$ ;  $D/Ti = 2.0-20$ ;  $Cl/Ti = 6-100$

and wherein said inert solid I is in a quantity ranging from 0 to 95%,

with protic organo-oxygenated compound  $D_p$ , in such a quantity that the molar ratio  $D_p/D$  ranges from 0.1 to 1.2, until equilibrium is reached.

28. The process according to claim 27, wherein said solid precursor is characterized by the following ratios:

$Mg/Ti = 1.5-10$ ;  $D/Ti = 4.0-12$ ;  $Cl/Ti = 10-30$

and said inert solid I is in a quantity ranging from 20 to 60% by weight with respect to the total weight of the precursor.

29. The process according to any of the previous claims 27

and 28, wherein the molar ratio  $D_p/D$  in said step ranges from 0.2 to 1.2.

30. The process according to any of the previous claims from 27 to 29, wherein said reaction is carried out at a temperature ranging from 40 to 100°C, for a period  
5 varying from 5 minutes to 5 hours.

31. The process according to the previous claim 30, wherein said reaction is carried out at a temperature ranging from 60 to 80°C, for a period of 5 to 60 min-  
10 utes.

32. A catalyst for the (co)polymerization of ethylene, which is obtained by means of contact and reaction of said solid component according to any of the previous claims from 1 to 13, with a co-catalyst comprising a  
15 hydrocarbyl compound of a metal selected from Al, Ga, Mg, Zn and Li.

33. The catalyst according to claim 32, wherein the atomic ratio between the metal in the co-catalyst and titanium in the solid component of catalyst ranges from  
20 10:1 to 500:1 and preferably from 50:1 to 200:1.

34. The catalyst according to claim 32 or 33, comprising titanium, magnesium, aluminum and chlorine, wherein said co-catalyst comprises an alkylic organometallic compound of aluminum.

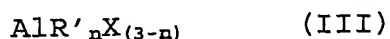
25 35. The catalyst according to claim 34, wherein said or-



ganometallic compound of aluminum is selected from aluminum tri-alkyls containing from 1 to 10 carbon atoms in each alkyl group.

36. The catalyst according to any of the claims from 32 to 35, wherein the contact between the solid component and co-catalyst is obtained *in situ* in the polymerization reactor.

37. The catalyst according to any of the claims from 32 to 36, wherein said solid component is activated before contact with said co-catalyst, by reaction with an aluminum alkyl or alkyl chloride represented by the following general formula (III):



wherein: R' is a linear or branched alkyl radical containing from 1 to 20 carbon atoms, X is selected from H and Cl, preferably Cl, and "n" is a decimal number having values ranging from 1 to 3, preferably from 2 to 3;

in such a quantity that the Al/(D+D<sub>p</sub>) ratio between the aluminium moles in said compound having formula (III) and the total of D and D<sub>p</sub> moles in said solid component, ranges from 0.1 to 1.5.

38. The catalyst according to claim 37, wherein said R' in formula (III) is a linear or branched aliphatic radical, having from 2 to 8 carbon atoms.

39. The catalyst according to anyone of the previous claims 37 and 38, wherein said  $\text{Al}/(\text{D}+\text{D}_p)$  ratio ranges from 0.2 to 1.3, preferably from 0.3 to 1.0.

40. The catalyst according to any of the previous claims from 37 to 39, wherein said solid component is activated in two successive steps by reaction in the first step with an aluminum trialkyl ( $n = 3$  in formula (III)), and in the second step with an aluminum dialkyl chloride ( $n = 2$ ,  $X = \text{Cl}$ , in formula (III)), in such a quantity that the overall molar ratio  $\text{Al}/(\text{D}+\text{D}_p)$  ranges from 0.1 to 1.3, preferably from 0.4 to 1.1.

41. The catalyst according to claim 40, wherein, in said first step the molar ratio  $\text{AlR}_3/(\text{D}+\text{D}_p)$  ranges from 0.1 to 0.4 and in the second step the molar ratio  $\text{AlR}_2\text{Cl}/(\text{D}+\text{D}_p)$  ranges from 0.2 to 0.6.

42. A process for the (co)polymerization of ethylene, comprising reacting ethylene and optionally at least one alpha-olefin, under suitable polymerization conditions, in the presence of said catalyst according to any of the previous claims from 32 to 41.

43. The process according to claim 42, carried out in gas phase with the fluid-bed method, wherein a gaseous stream of ethylene and optional alpha-olefin is reacted in the presence of a sufficient quantity of catalyst, at a temperature ranging from 70 to 115°C,

and at a pressure ranging from 500 to 1000 kPa.

44. The process according to the previous claim 43, wherein said stream is introduced from the bottom of the polymerization reactor, partially comprising a stream in liquid form.

45. The process according to anyone of claim 43 and 44, in the presence of a catalyst according to any of the previous claims from 37 to 41.

46. The process according to any of the preceeding claims from 42 to 45, wherein the molar ratio with ethylene ranges from 0.1 to 1.0.

47. The process according to any of the preceeding claims from 42 to 46, wherein said  $\alpha$ -olefin is selected from 1-butene, 1-hexene and 1-octene and is in such a quantity that the molar ratio with ethylene ranges from 0.1 to 0.4.

48. The process according to any of the preceeding claims from 42 to 47, for obtaining linear polyethylene having a density ranging from 0.915 to 0.950 g/ml,

49. The process according to any of the preceeding claims from 43 to 47 for obtaining linear polyethylene having a density lower than 0.915 g/ml, preferably ranging from 0.900 to less than 0.915 g/ml, comprising the copolymerization in gas phase of a gaseous mixture including ethylene and at least one alpha-olefin having

from 4 to 10 carbon atoms.

50. The process according to claim 49, wherein the gaseous mixture of ethylene and the at least one alpha-olefin is reacted in the presence of a sufficient quantity of catalyst, at a temperature ranging from 70 to 95°C, and a pressure ranging from 500 to 1000 kPa.

51. The process according to any of the previous claims 49 and 50, wherein said alpha-olefin is selected from 1-butene, 1-hexene and 1-octene, and is in such a quantity that the molar ratio with respect to ethylene ranges from 0.1 to 0.4.

52. The process according to any of the previous claims from 42 to 51, wherein said catalyst is formed *in situ* inside the reactor.

53. The process according to any of the previous claims from 42 to 52, wherein said linear polyethylene has a weight average molecular weight  $M_w$  ranging from 20,000 to 500,000 and a MWD ( $M_w/M_n$ ) distribution ranging from 2.5 to 4.